

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵: C07C 67/38, B01J 31/24, C07C 69/24	A1	(11) International Publication Number: WO 94/18154 (43) International Publication Date: 18 August 1994 (18.08.94)
(21) International Application Number: PCT/EP94/00379 (22) International Filing Date: 7 February 1994 (07.02.94) (30) Priority Data: 93200360.1 9 February 1993 (09.02.93) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: DRENT, Eit; Badhuisweg 3, NL-1031 CM Amsterdam (NL). PELLO, Dennis, Humphrey, Louis; Badhuisweg 3, NL-1031 CM Amsterdam (NL). HASSELAAR, Melis; Badhuisweg 3, NL-1031 CM Amsterdam (NL).		(81) Designated States: CA, CN, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: CARBONYLATION PROCESS (57) Abstract The invention provides a process for the carbonylation of ethylenically unsaturated compounds by reaction with carbon monoxide and a co-reactant in the presence of a substantially non-acidic catalyst system based on a palladium compound and a bidentate ligand of the formula (I): $R^1R^2M^1RM^2R^3R^4$ wherein M^1 and M^2 independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent organic bridging group, R^1 , R^2 , R^3 and R^4 independently represent substituted or non-substituted aliphatic groups, with the proviso that R^1 together with R^2 , and/or R^3 together with R^4 represent a bivalent cyclic group with at least 5 ring atoms whereby the two free valencies are linked to M^1 or M^2 , respectively. In addition, the invention provides catalytic compositions comprising: a) a palladium compound; b) a bidentate ligand of the formula (II): $R^1R^2PRPR^3R^4$ wherein R is a bivalent organic bridging group containing from 1 to 10 atoms in the bridge and R^1 , R^2 , R^3 and R^4 independently represented substituted or non-substituted aliphatic groups, with the proviso that R^1 together with R^2 and/or R^3 together with R^4 represent a bivalent cyclic group with at least 6 ring atoms whereby the two free valencies are linked to the phosphorus atom(s) and c) a basic compound.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

CARBONYLATION PROCESS

The invention relates to a process for the carbonylation of ethylenically unsaturated compounds by reaction with carbon monoxide and a co-reactant in the presence of a palladium-containing catalyst system.

5 Various carbonylation reactions of this type are disclosed in EP-A-0,495,547. In the process described in that document, an optionally substituted olefinically unsaturated compound is reacted with carbon monoxide and a variety of co-reactants in the presence of a catalyst system comprising: a source of palladium cations; a
10 source of bidentate ligands; and a source of anions, wherein the ligands are selected from diphosphines having the general formula $Q^1 Q^2 P X P Q^3 Q^4$, wherein the groups Q^1 , Q^2 , Q^3 , and Q^4 independently represent an optionally substituted aliphatic group, or Q^1 together with Q^2 , and/or Q^3 together with Q^4 , represent an optionally
15 substituted bivalent aliphatic group, and X represents a bivalent bridging group containing from 1 to 10 atoms in the bridge. As anion source, preferably a protonic acid is selected. Preference is in particular given to sources of non- or weakly-coordinating anions, i.e. anions which do not or only weakly coordinate with the
20 palladium cation.

Whilst the process disclosed in EP-A-0,495,547 in general provides the desired product in good yield and with high selectivity, it has been experienced that the reaction rate in some instances leaves room for improvement. Efforts have therefore continued to
25 achieve an increase in reaction rate, without impeding other factors such as selectivity or catalyst stability.

Surprisingly it has now been found, that by using a substantially non-acidic catalyst system and by selecting a specific category of bidentate ligands, the rate of a number of carbonylation reactions is significantly increased.
30

- 2 -

The invention may be defined as relating to a process for the carbonylation of ethylenically unsaturated compounds by reaction with carbon monoxide and a co-reactant in the presence of a substantially non-acidic catalyst system based on a palladium compound and a bidentate ligand of the formula



wherein M^1 and M^2 independently represents a phosphorus, arsenic or antimony atom, R represents a bivalent organic bridging group, R^1 , R^2 , R^3 and R^4 independently represent substituted or non-substituted aliphatic groups, with the proviso that R^1 together with R^2 , and/or R^3 together with R^4 represent a bivalent cyclic group with at least 5 ring atoms whereby the two free valencies are linked to M^1 or M^2 , respectively.

It is believed that the carbonylation reactions according to the invention proceed under the influence of an active catalyst system containing palladium cations, in complex coordination with a bidentate ligand.

The palladium cations may originate from salts, for example salts derived from nitric acid, sulphuric acid, and sulphonic acids, such as p-toluenesulphonic acid, methanesulphonic acid or trifluoromethanesulphonic acid. Preferably, a palladium salt of a carboxylic acid is used, for example acetic acid, trifluoroacetic acid or propionic acid. If desired, the metallic element or a zero valent palladium complex, e.g. with carbon monoxide can be used. However, this will require the presence of a protonic acid and it will be appreciated that the amount thereof has to be selected very carefully, in order to avoid that an acidic catalyst system results.

In the bidentate ligands of formula (I), both M^1 and M^2 preferably represent phosphorus atoms. R preferably represents a bivalent organic bridging group, containing from 1 to 10 atoms in the bridge. More preferably, R represents an alkylene group containing from 1 to 4 atoms in the bridge. In general the bridging group consists of carbon and hydrogen atoms only, but it may also comprise a carbon chain, interrupted by a heteroatom, such as an

- 3 -

oxygen atom. In particular preferred are ligands of formula (I) in which R represents an ethylene group.

The cyclic group(s) formed by R^1 together with R^2 , and/or R^3 together with R^4 comprise at least 5 ring atoms, in particular from 5 6 to 9 ring atoms. As a rule they comprise only carbon atoms as ring atoms, but cyclic groups containing 1 or 2 heteroatoms in the ring, such as oxygen- or nitrogen-ring atoms are not precluded. Very suitable are bivalent cyclic groups, whereby the ring consists of 7 or, preferably, 8 carbon atoms. The two free valencies may 10 occur at adjacent carbon ring atoms, or at two carbon atoms which are further apart. Examples of suitable cyclic groups are: 1,2-cyclooctylene, 1,3-cyclooctylene, 1,4-cyclooctylene, 1,5-cyclooctylene, 1,4-cyclohexylene, 1,3-cycloheptylene and 1,4-cycloheptylene groups. Mixtures of bidentate ligands may be used as, 15 well, whereby R^1 together with R^2 represent various cyclic groups and R^3 and R^4 represent either non-cyclic aliphatic groups or R^3 , together with R^4 represent cyclic groups which may be the same as or different from the cyclic group represented by R^1 and R^2 . Examples of suitable bidentate ligands selected from the [4.2.1] 20 and/or [3.3.1] isomers of 1,2-bis(9-phosphabicyclononyl)ethane and 1,2-bis(9-phosphabicyclononyl)propane; 1,3-bis(9-phosphabicyclo-[3.3.1.]nonyl)propane and 1,3-bis(9-phosphabicyclononyl)propane; and 1-dialkylphosphino-2-P-(9-phosphabicyclononyl)ethane. If R^1 and R^2 , or R^3 and R^4 do not represent a bivalent cyclic group, they 25 suitably represent an optionally substituted alkyl, preferably a C_{1-6} alkyl, or monovalent cycloalkyl, preferably a cyclo C_{5-10} alkyl group. Examples of suitable alkyl groups are methyl, ethyl or butyl groups. Suitable cycloalkyl groups are for example cyclohexyl or cyclooctyl groups.

30 The ratio of number of moles of ligands of formula (I) per gram atom of palladium is preferably in the range of from 0.5 to 10, most preferably in the range of from 1 to 3.

The process according to the invention is preferably carried out in the presence of a basic compound. It is believed that the 35 presence of a basic compound not only ensures that the catalyst

- 4 -

system remains non-acidic during the process, but also favourably affects the catalytic activity. Accordingly, it is considered likely, that at least part of the quantity of basic compound participates in the catalyst system. Suitable basic compounds, in particular, are nitrogen bases, preferably nitrogen-containing compounds wherein the nitrogen atom(s) is (are) only linked to atoms, other than hydrogen. Examples of suitable nitrogen bases are trialkylamines, preferably tri-C₁₋₆ alkyl-amines, especially triethylamine, tripropylamine, tri-n-butylamine and tri-tert.butylamine. Examples of suitable cyclic amines are pyridine and alkylpyridines, e.g. (C₁₋₄ alkyl)pyridines, such as 2-methylpyridine, 3,4-dimethylpyridine and 1,10-phenanthroline. The amount of basic compound is not critical and may vary between wide limits. Usually a molar amount of basic compound is selected in the range of from 1 to 100, preferably in the range of from 1 to 20, per gram atom of palladium. Conveniently, the amount of catalyst system is relatively small. Preferred amounts are in the range of 10⁻⁷ to 10⁻¹ gram atom palladium per mole of ethylenically unsaturated compound, more preferably in the range of 10⁻⁶ to 10⁻² on the same basis.

Catalyst compositions comprising:

a) a palladium compound;

b) a bidentate ligand of the formula



wherein R is a bivalent organic bridging group containing from 1 to 10 atoms in the bridge and R¹, R², R³ and R⁴ independently represent substituted or non-substituted aliphatic groups, with the proviso that R¹ together with R² and/or R³ together with R⁴ represent a bivalent cyclic group with at least 6 ring atoms, whereby the two free valencies are linked to the phosphorus atom(s); and

c) a basic compound, are novel.

Accordingly, the invention also relates to these novel catalyst compositions. The invention in particular relates to catalyst compositions comprising: a palladium compound; a bidentate ligand of formula (II), wherein R¹R²P and R³R⁴P each represent the [4.2.1]

and/or [3.3.1] isomer of a 9-phosphabicyclononyl group and R represents an ethylene group; and pyridine or a trialkylamine.

The bidentate ligands of formula (II) may be prepared by known techniques such as those described in British Patent Specification
5 No. 1,127,965.

The ethylenically unsaturated compound may have one or more double bonds. It is preferably an olefin having from 2 to 20 carbon atoms per molecule. The unsaturated bond(s) may be internal or, preferably, terminal. In particular preferred are olefins having
10 from 2 to 8 carbon atoms per molecule, such as ethene, propene, butene-1, hexene-1 and octene-1.

In the ethylenically unsaturated compound one or more hydrogen atoms may have been substituted by other atoms, such as halogen atoms or by groups of atoms, such as hydroxyl groups, cyano groups.
15 such as methoxy or ethoxy groups, or amino groups such as dimethyl- and diethyl-amino groups.

Another preferred category of ethylenically unsaturated compounds, consists of unsaturated esters of carboxylic acids and esters of unsaturated carboxylic acids. For example, the starting
20 material may be a vinyl ester of a carboxylic acid such as acetic acid or propionic acid, or it may be an alkyl ester of an unsaturated acid, such as the methyl or ethyl ester of acrylic acid or methacrylic acid.

Suitable co-reactants in the process of the invention include
25 compounds comprising a nucleophilic moiety and a mobile hydrogen atom. Examples are mono- and dihydric alkanols, such as methanol, ethanol, n-butanol, ethylene glycol, isopropanol, butanediols and hexanol-1, and amines, such as ethylamine and diethylamine. Alkanols with 1 to 6 carbon atoms per molecule and alkanediols with 2
30 to 6 carbon atoms per molecule are preferred. n-Butanol-1, methanol and 1,4-butanediol are especially preferred. The use of these compounds as co-reactants enables the production of valuable carbonylation products, such as methylpropionate, butylpropionate and 1,4-diacetoxy butanes.

These compounds are of commercial interest and may be used as solvents and in flavouring compositions and perfumes. In the process of the invention the ethylenically unsaturated compound, or the co-reactant may be used in excess and, accordingly, may serve
5 as solvent during the reaction. It is also possible to perform the reaction in the presence of an additional liquid diluent, in particular when the reactants are used in stoichiometric amounts. Suitable diluents are for example polar, aprotic compounds, such as ketones or ethers. Preferred diluents are tetrahydrofuran and the
10 dimethylether of diethyleneglycol (diglyme).

If so desired, the reaction may be performed in the further presence of a promoter, such as a drying agent. Suitable drying agents include acetals, such as dimethyl-acetal of acetone, ketals and the like. A preferred drying agent is trimethyl orthoformate.

15 The carbonylation reaction is conveniently carried out at moderate temperatures, generally being in the range of from 30 to 200 °C, preferably in the range of from 50 to 150 °C. Reaction pressures may be atmospheric or superatmospheric. In particular pressures in the range of from 5 to 70 bar are preferred. Higher
20 pressures are not precluded, but usually do not provide advantages.

The invention will be illustrated by the following examples.

Examples I-XI

The experiments were carried out by each time charging a 250 mL magnetically-stirred "Hastelloy C" (trade mark) autoclave
25 with 0.25 mmol palladium(II)acetate, 0.6 mmol of a diphosphine ligand, 50 mL of an alkanol co-reactant and, where applicable, one or more additives. The autoclave was flushed with a 1.5:1 molar mixture of carbon monoxide and ethene and pressurized to a total pressure of 50 bar. The autoclave was then sealed and the mixture
30 was heated to the desired reaction temperature. The reaction was continued to complete ethene conversion and subsequently the reaction mixture was cooled to room temperature and the pressure released. The ligand, co-reactant, additive (if any), reaction temperature and average hourly rate of ester formation are shown in
35 Table 1.

- 7 -

The abbreviations used in the table have the following meanings:

BPBNP = 1,3-bis(9-phospha-bicyclononyl)propane
MBPBNE = 1-methyl-1,2-bis(9-phospha-bicyclononyl)ethane
5 1,2-bis(9-phosphabicyclononyl)propane
BPBNE = 1,2-bis(9-phospha-bicyclononyl)ethane
DMP = 3,4-dimethylpyridine(lutidine)
Phen = 1,10-phenanthroline
BBA = 2,6-di(sec.butoxy)benzoic acid
10 TEA = triethylamine
TMF = trimethyl orthoformate

The product obtained in Example V was methylpropionate; in the other examples n-butylpropionate was obtained. The selectivity with respect to the ester was more than 99%. From the results of Examples I, II and III it can be seen that by the presence of a basic compound, the rate is increased and that a further increase in rate is obtained by adding a drying agent. Likewise, comparing the results of Examples IV, VI, VII and VIII, an increase in rate is observed by adding a drying agent or a basic compound. The effect of adding a drying agent is further illustrated by comparing the results of Examples IX and X.

Example B (not according to the invention, for comparison only)

An experiment was carried out, substantially under the conditions as described for Example IV with the differences that the reaction temperature was 130 °C, instead of 125 °C and that as ligand 1,2-bis(dicyclohexylphosphino)ethane was used. The rate was 30 mol/gat Pd.h.

Example C (not according to the invention, for comparison only)

An experiment was carried out, substantially under the conditions as described for Example II, with the difference that as ligand 1,3-bis(di-sec.butylphosphino)propane was used. The rate was 50 mol/gat Pd.h.

- 8 -

Table 1

Example	Ligand	Additive (mmol)	Alkanol (mL)	Temperature (°C)	Rate (mol/gat Pd.h)
I	BPBNP	-	n-butanol 50	125	35
II	"	DMP 10	"	137	85
III	"	"	"	137	330
		TMF 5 mL			
IV	BPBNE	-	"	125	520
V	"	-	methanol 50	125	490
VI	"	TMF 1 mL	n-butanol 50	125	600
VII	"	Phen 1	"	125	630
VIII	"	Phen 2.5	"	125	1150
		TMF 1 mL			
A*	"	BBA 10	"	120	360
IX	"	TEA 10	"	133	275
X	"	"	"	133	725
		TMF 5 mL			
XI	"	DMP 10	"	135	1160
		TMF 5 mL			

* not according to the invention, for comparison only

Example XII

An experiment was carried out, whereby the autoclave (magnetically stirred, 250 mL, "Hastelloy C") was charged with 0.25 mmol palladium (II) acetate, 0.6 mmol of a diphosphine ligand (BPBNP as defined above), 10 mmol of triethylamine, 5 mL of trimethyl orthoformate, 50 mL of methanol and 20 mL of n-octene-1. The autoclave was flushed and pressurized with carbon monoxide to a pressure of 30 bar. The mixture was heated to 130 °C. The reaction was continued to complete octene conversion and subsequently the reaction mixture was cooled to room temperature and the pressure released. The rate was 100 mol/gat Pd.h. The linearity of the formed methyl ester of nonanoic acid was 73%.

Example XIII

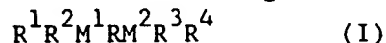
5 An experiment was carried out, substantially as described in Example XII, with the difference that instead of BPBNP as ligand BPBNE was used. (BPBNP and BPBNE are as defined above). The rate was 170 mol/gat Pd.h. The linearity of the formed methyl ester of nonanoic acid was 69%.

Example XIV

10 An experiment was carried out, substantially as described in Example I, with the difference that 40 instead 50 mL n-butanol was used, at a temperature of 130 °C and using MBPBNE instead of BPBNP as ligand. (BPBNP and MBPBNE are as defined above). The rate was 200 mol/gat Pd.h. The selectivity with respect to n-butylpropionate was more than 99%.

C L A I M S

1. A process for the carbonylation of ethylenically unsaturated compounds by reaction with carbon monoxide and a co-reactant in the presence of a substantially non-acidic catalyst system based on a palladium compound and a bidentate ligand of the formula



wherein M^1 and M^2 independently represent a phosphorus, arsenic or antimony atom, R represents a bivalent organic bridging group, R^1 , R^2 , R^3 and R^4 independently represent substituted or non-substituted aliphatic groups, with the proviso that R^1 together with R^2 , and/or R^3 together with R^4 represent a bivalent cyclic group with at least 5 ring atoms whereby the two free valencies are linked to M^1 or M^2 , respectively.

2. A process as claimed in claim 1, wherein M^1 and M^2 both represent phosphorus atoms.
3. A process as claimed in claim 1 or 2, wherein R represents a bivalent organic bridging group containing from 1 to 10 atoms in the bridge.
4. A process as claimed in any one of claims 1 to 3, wherein R represents an ethylene group.
5. A process as claimed in any one of claims 1 to 4, wherein the bivalent cyclic group represented by R^1 together with R^2 , and/or by R^3 together with R^4 , is a cycloalkylene group having from 6 to 9 ring atoms.
6. A process as claimed in claim 5, wherein R is linked to two phosphorus atoms, each of which participates in the [4.2.1] and/or [3.3.1] isomer of a 9-phosphabicyclononyl group.
7. A process as claimed in any one of claims 1 to 6, wherein the reaction is carried out in the presence of a basic compound.
8. A process as claimed in claim 7, wherein as basic compound pyridine, a substituted pyridine or a trialkylamine is used.

- 11 -

9. A process as claimed in any one of claims 1 to 8, wherein the reaction is carried out in the presence of a liquid diluent.

10. A process as claimed in claim 9, wherein as diluent an ether is used, in particular tetrahydrofuran or the dimethylether of diethylene glycol.

11. Catalyst composition comprising:

a) a palladium compound;

b) a bidentate ligand of the formula



wherein R is a bivalent organic bridging group containing from 1 to 10 atoms in the bridge and R^1 , R^2 , R^3 and R^4 independently represent substituted or non-substituted aliphatic groups, with the proviso that R^1 together with R^2 and/or R^3 together with R^4 represent a bivalent cyclic group with at least 6 ring atoms whereby the two free valencies are linked to the phosphorus atom(s) and

c) a basic compound.

12. Catalyst composition as claimed in claim 11, wherein R^1R^2P and R^3R^4P each represent the [4.2.1] and/or [3.3.1] isomer of a 9-phospha-bicyclononyl group and wherein the basic compound is pyridine, a substituted pyridine or a trialkylamine.

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 5 C07C67/38 B01 31/24 C07C69/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 5 C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 495 547 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 22 July 1992 cited in the application see page 5, line 23 - line 37 see page 7, line 48 - line 53 see page 9, line 23 - line 31 see page 23 - page 25; claims 1-6,28,30,34,35 ---	1-6,9-12
Y	EP,A,0 055 875 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 14 July 1982 see page 2, line 16 - page 29 see page 7, line 15 - line 21 see page 9, line 13 - line 25 see page 18 - page 19; claims --- -/--	1,2,9-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

31 May 1994

Date of mailing of the international search report

- 3. 05. 94

Name and mailing address of the ISA
 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+ 31-70) 340-3016

Authorized officer

Kinzinger, J

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with page, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP, A, 0 441 446 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 14 August 1991 see page 2, line 38 - line 52 see page 5, line 1 - line 44 see page 6, line 15 - line 22 see page 7, line 35 - line 58 see page 13; example 5 see page 17; claims 1,2,5,6,9-14 -----	1,2,9-11

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0495547	22-07-92	CA-A- 2059233	16-07-92
		CA-A- 2059236	16-07-92
		CN-A- 1063277	05-08-92
		EP-A- 0495548	22-07-92
		JP-A- 5058949	09-03-93
		JP-A- 4334340	20-11-92
		US-A- 5210280	11-05-93
EP-A-0055875	14-07-82	AU-B- 544588	06-06-85
		AU-A- 7915982	15-07-82
		CA-A- 1177845	13-11-84
		JP-B- 5021902	25-03-93
		JP-A- 57134437	19-08-82
EP-A-0441446	14-08-91	JP-A- 4215852	06-08-92
		US-A- 5124300	23-06-92
		US-A- 5166411	24-11-92